An Investigation of Manometers, of Small Pore, for Use

in the Measurement of Osmotic Pressure.

DISSERTATION

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John Lattimore Carpenter

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C O N T E N T S

Page

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OSMOTIC PRESSURE.

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1.   Review of Former Work.

Throughout the ten or more years of investigation of
osmotic pressure in this laboratory a major portion of the
time has been spent in the detection and elimination of sources
of error. In order that the problem might be attacked upon a
secure basis, the following factors must become known and re-
liable quantities, viz: a suitably strong semi-permeable mem-
brane; an effective method for depositing the same; a cell of
fine texture, suitable porosity and at the same time possessing
great strength of wall; baths accurately and automatically re-
gulated as to temperature; and finally, manometers - of a type
convenient to manipulate for registration of the pressure ex-
erted within the cell. Examination of the published work will
reveal how elaborate and perfect the system has come to be.

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1. Earlier papers will be found in Am. Ch. Jr., 28,1; 29,173;
32,93; 34,1; 36,1 & 39; 37,324,425,558; 38,175; 39,667; 40,1,194,
266,325; 41,1,92,257; 45,91.

In fact all the larger difficulties have been disposed of rather satisfactorily except the manometer factor.

Sufficiently accurate manometers for the measurement of the temperature coefficient of osmotic pressure have been in use for three years and their preparation has been described.[2] But it was realized that these instruments had constant error factors - though of uncertain magnitude - and it was with difficulty that an adequate number of the instruments agreeing sufficiently well among themselves were finally obtained. By the methods of manometer preparation formerly used one was by no means certain whether he would obtain a "good" instrument. The worker was constantly fearing the worst and in the majority of cases his fears were realized. However, a series of manometers came into hand which agreed closely, and these were chosen for the measurements.

These manometers have been prepared substantially, as follows:- the capillary[3] tubes were chosen with care, extra effort being made to find those of most uniform bore; the tubes were then calibrated carefully from a scratch on the tube near the bottom of that portion which would be filled with gas .

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2. Am. Ch. Jr., 40,325.

3. The term "capillary" referred to manometer tubing in this paper means a tube varying in diameter from 0.4 m.m. to 0.8 m.m.

Curves were plotted and the irregularities expressed in "cali-
bration units." Next the capillary depression of the tube was
determined at some point, and then the tube was carefully clean-
ed again, dried and filled in the customary manner with nitro-
gen. The next step in the procedure was the determination of
the volume of gas, expressed in calibration units, contained in
the closed manometer. Three methods were used - two differing
only slightly from each other. One method was to place the
manometer in a steel block and calculate the volume from the
known volume of a "standard" manometer. The "steel block" is
nothing more than a strong reservoir with receptacles for three
manometers and plungers with which to secure a wide range of
pressures. From the known volume of the "standard" one could
calculate the pressure its gas volume was under. Then with the
proper corrections applied to the manometer under comparison
one could calculate the volume of gas inclosed at $0-760.^{mm}$ This
method soon fell under suspicion for reasons not fully under-
stood at the time - these will be presented later. The other
method consisted of the open "side tube" method. The "side
tube" consisted of a portion of the same capillary from which

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4. The "calibration unit" is the average volume of each mille-
metre of the calibrated tube, and is calculated from the weight
of a thread of mercury which fills the whole length of the
capillary.

the manometer was made. The purpose was to eliminate capillary
depression effects. If the said tube was substituted in the
steel block in place of the "standard manometer" the pressure on
the manometer under examination was easily obtained. It would
be the sum of the height of the mercury column in the side tube,
above that in the manometer, plus the barometric pressure. Know-
ing the pressure and observing the volume of the gas in the
manometer and keeping the latter at a strictly constant temper-
ature, it is only necessary to apply the gas law equations to
find the volume under standard conditions. A modification of
the "side tube" method was to use a tape wound rubber tube as
the connecting reservoir between "side tube" and manometer.
This economized time, and is equally accurate. After a number
of observations had been made at different pressures on one man-
ometer, under examination, the average value of these was as-
sumed to closely approximate its volume. The final test of the
manometer however came after it had registered constant pres-
sure when set up in solutions of known pressure capacity - i.e.
in terms of the manometers chosen before as probably the most
accurate ones. That there was error in the absolute gas volumes
of these manometers, and therefore error in the pressures they
registered, was recognized. But these errors were small and

of such a nature that they exercised negligible effect upon the
ratio expressing relation of osmotic pressure to temperature or
in other words the temperature coefficient.

A New Type of Manometer, and Discussion of the Same.

However, when the determination of absolute osmotic pressure
is to be considered - or in other words the relation of concen-
tration to pressure, these errors assume an altogether serious
aspect. And while the errors are small, and the labor of elim-
inating them is tedious and time consuming, still the end hoped
for is worthy, or even necessary. The work herein described
has been an effort to eliminate as far as posible this last
error source - the manometer error factor.

With a manometer of large volume the majority of error
sources are no larger than in those of small volume. Hence in
those of large volume the percentage error would be greatly
reduced. With this idea in mind a new type of manometer was
devised. Figs. I and II show the old and new type respectively.
The type shown in Fig. II has a tube of large bore scaled be-
tween the two portions of small bore. The purpose of this is
to furnish a large volume without unduly lengthening the in-
strument. These large tubes are so selected as to length and
bore that the instruments may be used only above certain con-
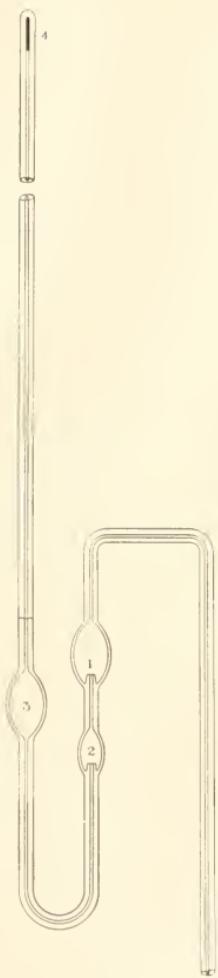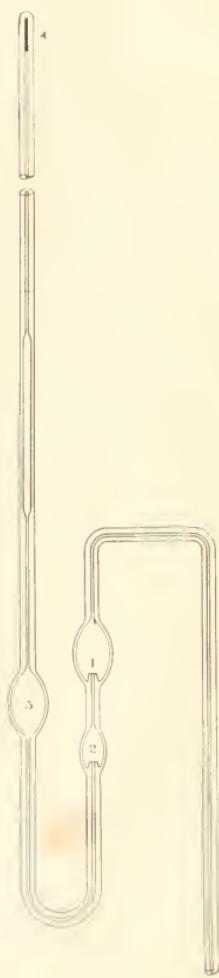
Fig. I.   Fig. II

centrations, that is, a solution must exert sufficient pressure
to sustain the mercury at a point several millimetres above
the joint of the enlarged portion of the tube and the capillary
above. The pressures necessary vary from 3 or 4 to 20 atmos-
pheres for different manometers.

The capillary tubes were selected with the usual
care and put into the hands of an expert glass blower. They
were returned as straight tubes, extending in length a few cen-
timetres below bulb 3 and not sealed at the top as shown at
4. These tubes were carefully annealed, allowed to rest undis-
turbed for some months before calibration. These tubes were
then carefully calibrated by the usual method in use in this
laboratory. [5] From Fig. II it may be observed that small marks
cross the capillary a few millimetres above bulb 3 and the en-
larged portion of the tube. These marks are known as the "lower
scratch" and "upper scratch" respectively, and the small cap-
illaries above them are known as the "short" and "long" capilla-
ries respectively. The "long capillary" was first calibrated
and the "calibration unit" determined. Next the "short capil-
lary" was calibrated and its curve plotted in terms of the long

5 This work was done by Dr. Holland.

capillary's calibration unit. Now a thread of mercury was run
into the enlarged portion of the tube until it filled the tube
from the upper scratch to some point certainly within the cal-
ibrated portion of the lower capillary. The length was ob-
served, the temperature likewise and the mercury was run out
and weighed. From the data in hand the total volume between
scratches was obtained, and this in turn was expressed in the
calibration unit of the long capillary. This latter operation
was all gone over in duplicate by the writer, and the values ob-
tained agreed very precisely with the former determinations.

DETERMINATION OF CAPILLARY DEPRESSION

(a) Purification of Mercury.

The next examination to be carried out was a detailed
one for capillary depression. For this purpose and also for
filling the manometers, a supply of very pure mercury was neces-
sary. The smallest amount of impurity either dissolved or me-
chanically held is well known to seriously hamper the free flow
of mercury through tubes of small bore. Hence the necessity of
very pure material. This had been previously prepared, and the
preparation had best be described here. To obtain pure mercury
is not such simple matter as might appear to the inexperienced.

Too great care cannot be exercised in its preparation. A high grade mercury was obtained from dealers and was subsequently treated by the writer in the following manner, (1) about four to six pounds were placed in a long necked hard glass receiving bulb. This had fitted into the neck a two hole cork stopper carrying ~~covering~~ two glass tubes, one of which extended below the surface of the mercury and opened into the air without, the other extended just below the stopper and at the other end was attached to a pump. The bulb was placed on a sand bath and heated to the boiling point of mercury for four to six hours, air being drawn through the entire time. The effect was surprising in that a large amount of impurity was oxidized and appeared on the surface as scum. (2) After cooling, and filtering through a paper perforated with pin holes, the now bright metal was introduced into and distilled through a vacuum still. This still was of a simple order, being made from a piece of Canius ~~series~~ combustion tubing. The supply reservoir of the still was an ordinary U-tube and from this the supply arm led up to the still proper. This tube was of such a length that by merely raising or lowering the U-tube one could adjust the length of the mercury column to meet barometric changes. The delivery tube was somewhat more than barometric length and hence always maintained a column of mer-

cury sufficient to offset atmospheric pressure. The upper por-
tion of the delivery tube was somewhat enlarged so that the
mercury would have greater condensing surface, and so that, in
falling, air was continually being trapped and carried out.
Once the still was in operation it gradually kept refining its
own vacuum. (3) The mercury was next washed by the method of
Lothar Meyer. Instead of ferric chloride solution however, a
two per cent nitric acid and two per cent mercurous nitrate solu-
tion was used. A very effective means of breaking the mercury
into fine globules was employed by the use of a silk bolting
cloth strainer. A half litre separatory funnel was flared
somewhat at the delivery stem and over this was bound a double
thickness of the cloth. On opening the stop cock and allowing
the mercury to enter it breaks into perhaps many thousands of
fine globules. In fact the separation is so effective that the
whole length of the two metre verticle tube, through which it
falls, is darkly and heavily clouded. This exposes an enormous-
ly large surface to the action of the acid and salt. Furthermore
the pouring was repeated 1000 times. By continually renewing the
solution it would seem quite safe to think that all those metals
which are volatile with mercury vapor, and hence had not been
left behind in process (2) would be removed. (4) After washing

with water, drying and filtering again, the mercury was finally redistilled through a second vacuum still. This still was of the same type as the one described above, but very much smaller. Before use in a manometer this mercury was filtered again, either through hard filter paper perforated with pin holes, or through a clean funnel drawn to a capillary at the end. The latter has the advantage that it offers no lent or dust to stick to the surface of the metal. An entirely satisfactory grade of mercury was thus obtained.

(b) Discussion of Capillary Depression.

The fact that it has been found most practicable to determine manometer volumes at low pressures caused the capillary depression factor to assume altogether important proportions. As mentioned above it was sought to escape this factor, in so far as it affected volume determinations, by the use of the "side tube" cut from the same piece of tubing as was the manometer. That it did not eliminate the error, but probably introduced one, will be shown later.

The procedure of determining the capillary depressions was very simple. A tube 40 m.m. in diameter and 25 c.m. long was used as the reservoir. This was sealed to a short piece of ordinary thick-walled barometer tubing, and manometer and

reservoir were connected by a suitablelength of tape-wound rub-
ber tubing filled with mercury. Before attaching the rubber
tube/the manometer the latter was supplied with a sufficient
quantity of the pure mercury to render it certain that the menis-
cus would be clean and the flow of the mercury free. The point
at which the meniscus stood could be varied at will by raising
or lowering the reservoir.

        This work was carried out in the "Manometer House"
which is kept at a constant temperature - and will be described
later. Hence the probability of error from fluctuating tem-
perature was avoided.

        Since the effect of capillary depression was most
serious as to its bearing upon volume determinations, and since
the meniscus in the manometer would stand somewhere in the short
capillary while its volume was being determined, it is at once
apparent that a detailed examination of that portion of the
manometer should be carried out. The capillary depressions
were ascertained at shorter intervals and with more precaution as
to tapping in the short capillary than in the long capillary.
Of course as the pressure increases in a manometer the capillary
depression error decreases, and indeed above a few atmospheres
becomes quite insignificant.

The tendency on the part of the mercury to lag in
the small capillary was overcome by tappers. These were the or-
dinary coils and hammer of small call bells, mounted upon weight-
ed standards. These could be easily placed in a suitable posi-
tion and controlled by a button on the outside of the manometer.
If it were left to these tappers alone to establish equilibrium
between the columns it frequently required more than an hour.
However the operator found that a preliminary tap or two on the
connecting rubber tube with a pencil would so hasten equilibrium
that only ten to fifteen minutes subsequent tapping by the
hammers was required.

It has been suggested that it is unnecessary to go
through the labor of experimentally determining the capillary
depression of small bore tubes. That instead of such experi-
mental determination the depressions could be calculated directly
from the surface tension value of mercury and the diameter of
the tube, expressed by the following equation.

$$dgh = \frac{2T}{r} \quad or \quad h = \frac{2T}{dgr},$$

where h would represent the depres-
sion, T the surface tension of mercury in dynes per centimetre, d the density of the
mercury at the temperature observed, g the gravita-
tional constant, and r the radius of the tube. Such a calculation
would be entirely satisfactory if one could be certain of the
values of T and r.

The value of T, however, is so strictly a function of the purity
and cleanliness of the mercury that it is not without risk that
the commonly accepted values are adopted. Furthermore, no scruple
must be spared in cleansing the capillary tubes. These two
factors - the mercury and the tube - place the investigator
in a dubious frame of mind as to how well some one else's value
for T will fit his own needs. Equally as serious, or probably
more serious, is the unreliability of the value for r at any
particular point. To determine the diameter of a capillary
tube exactly, at points very slightly removed from each other,
through any considerable length of a tube would involve an enor-
mous amount of time and labor. Slight irregularities only a
millimetre or two apart cause very marked differences in capil-
lary depression, hence it is not without grave risk that the
mean diameter through even a short distance may be adopted.
Nor is it in any measure safe to determine the capillary de-
pression at one or two points and adopt the mean as the true
depression for all points.

            The accompanying table I. will furnish some idea of
how variable depressions may be at points not remote from each
other, even though the tube has been chosen with utmost care.

The manometer was of the old type, as shown in Fig. I, and is, for certain laboratory convenience, designated M.5.

TABLE I

Distance above Scratch	Capillary Depression	Distance above Scratch	Capillary Depression
8.65	7.92	117.43	11.42
22.70	10.85	224.12	11.18
47.35	9.87	280.30	11.74
71.38	10.04	361.10	11.80
114.28	10.42	414.10	12.14

Now since at pressures ranging from 800 to 1000 millimetres constitute the limits between which one must determine the volumes of these manometers if open side is used, any considerable discrepancy in capillary depression would have a grave effect on the accuracy of the final result. In fact, at such low pressures, a difference of one millimetre amounts to a difference of about one calibration unit when the final volume is calculated. If in the case of manometer M.5 the depression had not been taken nearer the scratch than 22.7 millimetres, and the observations carried out from that point as tabulated, by former usage the mean value 11.05 of these last nine observations would have been adopted. If now the manometer had been filled with nitrogen, and sealed, and its volume under process of determination, unless sufficient pressure were brought to bear to bring the meniscus above 22.7 m.m. from the scratch

an uncertainty at least would be introduced as to the final
gas volume in the manometer. If the meniscus could not be
brought above 9 millimetres above the scratch, and if the mean
depression value of 11.05 were assumed to be the depression at
that point, an error of 11.05 - 7.92≡ 3.13 calibration units
would have resulted. The volume of this manometer, subsequently
determined, was 503.00 calibration units. An error of 3.13 cali-
bration units would have caused an error of about 0.62% on the
volume. While this error would have decreased as pressure in-
creased still it would have furnished sufficient discrepancy
from other instruments to stimulate distrust in its accuracy.
Hence, as has been stated above, very detailed determinations
of capillary depressions were made in the short capillaries of
the manometers, and careful though less detailed determinations
in the long capillary. Curves were plotted for depressions in
the same fashion as for calibration.

FILLING THE MANOMETERS

(a) The Preparation of the Nitrogen

The manometer tubes were now considered ready for
filling with nitrogen. To the stem below bulb 3, Figs. I and II,
the straight tube carrying bulbs 1 and 2 was sealed and subse-

quently bent as shown in the figure. To be quite satisfied as to the cleanliness of these tubes - now unfilled manometers - they were subjected to a third cleansing with sulphuric acid chromic acid mixture, washed out with distilled water, and finally washed several times with "conductivity water". They were then placed in a drying train, and dry air pumped through for not less than 18 hours.

[6]

Mention has been made, in a paper already published, of the fact that air was at one time used to fill the manometers and that nitrogen was subsequently adopted. When air, however carefully washed and dried, was used, there seemed ultimately to be a decrease in the volume of the gas in the manometer. This could be due to oxidation of impurity in the mercury - as oxidisable impurity might have been present. The adoption of nitrogen has eliminated that trouble. The preparation of the nitrogen was marked by the same care which was exercised in all the different steps of the work. The nitrogen was prepared from air in the following way: The air was drawn through a train of bottles containing alkali pyrogallate, continuing through a tube at red heat containing reduced copper, then on

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6   Loc. Cit.

through washbottles containing alkali pyrogallate and concen-
trated sulphuric acid respectively, thence through another tube
at red heat containing first copper oxide wire then reduced
copper gauze, thence through tubes of fused calcium chloride
and stick caustic alkali, and finally through a tube of resub-
limed phosphorous pentoxide distributed over asbestos fibre.
The whole train was filled, heated, and air drawn in for some time.
Then it was closed and allowed to stand for some hours in or-
der to give opportunity for a diffusion from all packed places
of any oxygen or other gas that could be separated out. After
reheating, and drawing in a current of air for some time and
allowing the nitrogen to waste, the reservoir was finally at-
tached and a supply of nitrogen collected.

(b) Filling and Closing the Manometer.

The method of filling the manometers was the same as that
used in former work, viz:- the mercury was first drawn into
bulbs 1, 2 and 3. Then the manometer is sealed at the top to
a stem from the nitrogen reservoir. The nitrogen is used to
wash the manometer free from air several times before it is
finally closed. After allowing the desired quantity of gas to
enter, the usual mercury thread is run in at the top, and the
manometer sealed off as described in a paper already referred
to.   Only one modification of the process was adopted.

Formerly, when the top of the manometer was being sealed off,
the short mercury thread immediately underneath the play of the
blow pipe flame often became so agitated - due to sudden vapori-
zation and condensation of its top portions - that globules
frequently became detached and trapped gas between themselves
and the main thread. This caused much trouble, and frequently
required reopening the manometer for their dislodgment. This
was remedied by simply softening the walls of the tube, some-
what above that portion at which the upper meniscus would stand,
and allowing the capillary to become constricted to very fine
bore. This measure hindered the rapid vibration back and forth
of the column and not a single accident was experienced in the
entire lot of manometers.

DETERMINATION OF GAS VOLUMES.

Since the object of this entire investigation was
the development of a reliable method for manometer construction,
and since up to this stage of the work no pains or time had
been spared for the sake of accuracy, it was necessary here to
hit upon the most reliable method of work also. Much care was
taken to arrange a bath which would conveniently accomodate all
the necessary apparatus, and at the same time be easily regulated
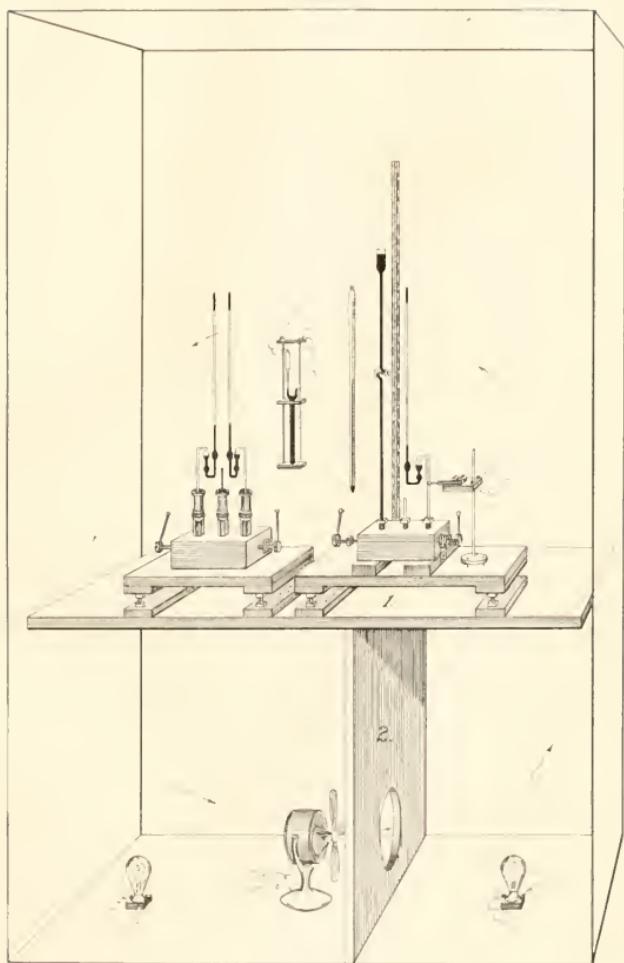
Fig. III.

at a constant temperature. This bath is known as the "manometer house". All the essential details are shown in Fig. III. In the figure (1) is a shelf on which is arranged all the instruments, such as the "steel block" the "brass block", the metre scale, the tappers, etc. This shelf rests on heavy brackets which are bolted to the heavy masonry of the wall behind. The thermo-regulator is hung from a bracket on the wall itself and is thus freed from the effects of the vibrations caused by the tappers when these are at work. Partition (2) merely serves to hold back the air and necessitates its being forced by the fan motor through the hole in the partition. The arrows show its direction of circulation. At each end of shelf (1) a 5 c.m. space allows the air to pass through the upper compartment. This bath is kept a few degrees above the temperature of the outside room - this latter being regulated roughly by a steam radiator or a gas stove. Control of temperature is maintained by the lamps shown in the figure - the lamps being controlled by the thermo-regulator above. In fact the system of the electric control of heat is identical with that in use in all the constant tempera-ture baths employed in this work. With this arrangement, fluc-tuation of temperature is kept well within 0.1 of a degree. More

Fig. IV.
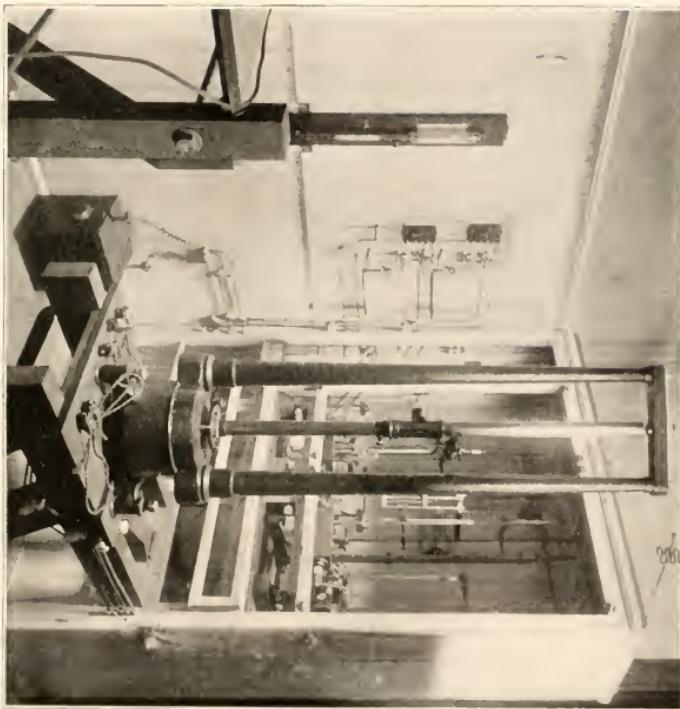
minute details of the manometer house are shown from Fig. IV.

The steel block, which has been previously described,
was originally designed for the determination of manometer gas
volumes against a "standard" manometer. The volume of the pro-
posed standard was dtermined at low pressures - but without
the precautions observed in the recent work. The idea was to
find the means of comparing other manometers under high pressure
with this one. Assuming that the original volume of the standard
was correct, the pressure it would be under at any position of
the meniscus could be easily calculated from the gas laws.
Further, if another manometer was in series with it, if proper
corrections were applied for the different heights of mercury,
the pressures must have been identical. From this pressure the
volume of the second manometer was in turn calculated. No sa-
tisfactory results were ever obtained by the "standard" manometer
method. At low pressures a different volume was always calcula-
ted than at high pressures. In Fig. V is shown a typical curve
for the "volume" of nitrogen in a manometer determined by this
method. Obviously, a volume curve of a closed manometer is a
straight line. Hence some constant error was affecting the
results. It is more probable that two factors were at work.
That one which was most effective under low pressure was prob-

Fig. V.

Typical Curve for Volume of a Manometer
Determined against the "Standard."

Volume in Calibration Units: Variations

Pressures in Atmospheres
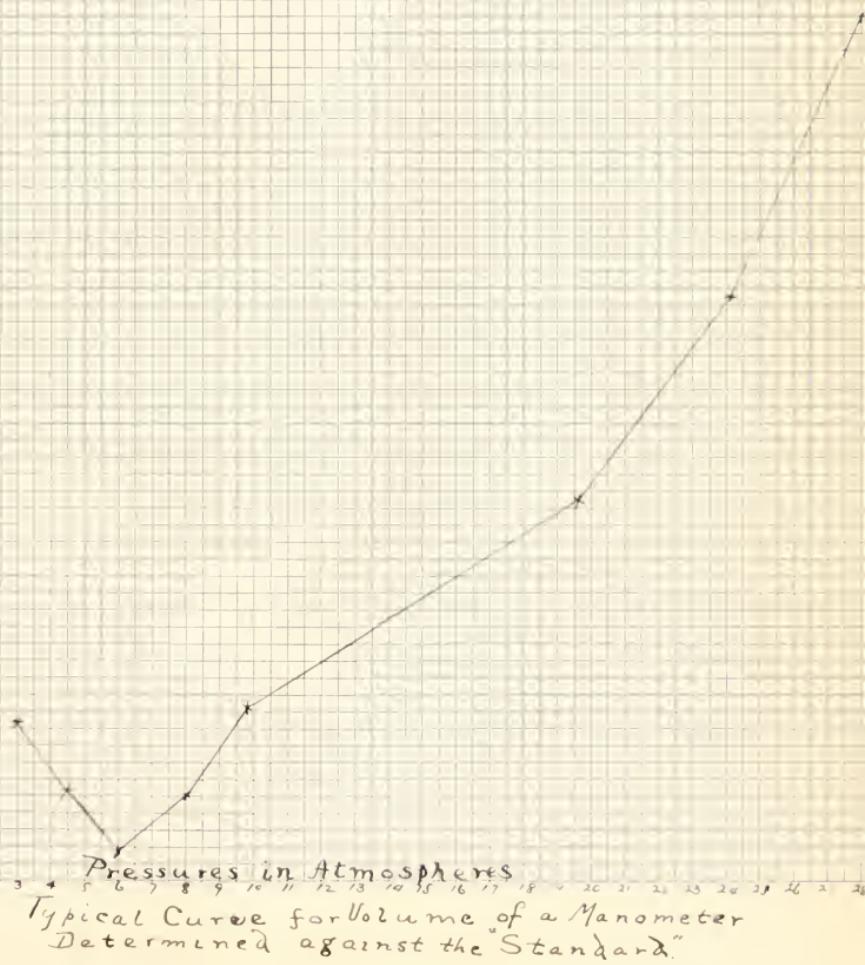
ably due to capillary depression. That under high pressure
appears to have been due to error in meniscus correction. The for-
mer error would decrease in importance as the pressure was in-
creased, while the latter error would increase in marked propor-
tion with increased pressure.

The proper meniscus correction has been a much mooted
question, and confession must be made that no method without
theoretical or practical objection is at hand. It is stated
that perfectly pure mercury leaves perfectly pure glass at an
angle of 148 degrees. The determination of such an angle would
not be difficult from a plane surface, or from a cylindrical sur-
face provided the arc of curvature of the latter was sufficient-
ly great to furnish a tube of such diameter that capillary
effects were overcome; but in a tube of very small bore such de-
termination would be a difficult matter. To assume that the menis-
cus in tubes of small bore is hemispherical , approaches the
true state of affairs but falls somewhat short of the mark.
However, we have found the correction based on such an assump-
tion to be perhaps the best available, and such correction has
been applied in this work. The method follows:- "Assuming that
the surface of a meniscus is similar in shape to half a sphere

and that the two surfaces of a double meniscus is equivalent to
an entire spherical surface the following conclusions may be
drawn: In a manometer there are a number of cylinders, each
capable of containing a definite number of cubical units, the
number of which would depend upon the position of the menisci
at the time a volume was included.

"Since the volume of a cylinder $= \pi R^2 h$, where $R =$
radius of the circular section, and h $=$ the height; and since
the volume of a sphere $= 4/3 \pi R^3$, and considering the sphere
inscribed in the cylinder, then the volume of the double menis-
cus is equivalent to the difference in volume of the cylinder
and the inscribed sphere. $\pi R^2 h - 4/3 \pi R^3 = x; h = 2R.$ Then
$\pi R^2 h = 2 \pi R^3 ; 2 \pi R^3 - 4/3 \pi R^3 = 2/3 \pi R^3 =$ volume of double
meniscus.

"Now since this expression above is in cubical units
and the volume of the manometers is expressed in linear units,
the former must be converted also into linear units.

"Now $2/3 \pi R^3 =$ volume in cubical units

$\pi R^2 =$ area in cross section

$2/3 \pi R^3$ divided by $\pi R^2 = 2/3 R =$ volume in
linear units. $2/3 R = 1/3 D.$ Hence, by determining the mean
diameter, the meniscus correction is at once obtained."

By a recent recalculation of a series of volume determinations on a manometer which was compared with the "standard", upon application of the revised meniscus correction, the curve shown in Fig. V was straightened out somewhat at higher pressures. This seemed to fix the trouble upon that factor. The importance of the meniscus correction may be seen from the following extract from a paper[7] on this work:" - - - in determining the temperature coefficient, the errors in the meniscus correction, if they are uniform, may be very large without seriously affecting the result; but when it is attempted to ascertain the relation of osmotic pressure to concentration, the case is very different, for then the pressures of all the various concentrations of solution are to be compared at fixed temperatures, and the meniscus corrections have consequently widely differing values. This is illustrated from the data taken from the record of a single manometer (No. 9). The meniscus correction (double) in this instrument is 0.17 calibration unit, and the volume of nitrogen under standard conditions of temperature and pressure is 454.14 calibration units. Column I in the table gives the weight normal concentration of the solutions; II, the pressures in atmospheres; III, the volume of the compressed nitrogen reduced to standard temperature; IV,

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7 Am. Ch. Jr., 45,237.

the corrections in fractions of an atmosphere for the double me-
niscus; V, the relative osmotic pressures, the pressures of the
0.1 normal solution serving as the unit. Column VI contains the
relative corrections for meniscus, the correction for the 0.1
normal solution serving as the unit. The temperature in all
cases is 25 degrees.

I	II	III	IV	V	VI
CONC.	OS. PRES:	VOL.NITROGEN	MEN. COR.:	REL.OS.PRES.:	REL.MEN.COR.
	ATMOS.	CAL UNITS	ATMOS.		
0.1:	2.635	141.15	0.00317	1.0000	1.0000
0.2:	5.139	80.69	0.01083	1.9503	3.4164
0.3:	7.738	55.59	0.02366	2.9366	7.4637
0.4:	10.295	42.41	0.04126	3.9070	13.0158
0.5:	12.947	34.01	0.06972	4.9135	21.9937
0.6:	15.620	28.37	0.09360	5.9275	29.5268
0.7:	18.436	24.11	0.12999	6.9928	41.0063
0.8:	21.258	20.97	0.17233	8.1055	54.3628
0.9:	24.126	18.53	0.22133	9.1558	69.8202
1.0:	27.076	16.54	0.27834	10.2755	87.8044

Particular attention is called to columns V and VI,
where it will be seen that, while osmotic pressure increased
a little over ten fold, the value of the meniscus correction in-
creased nearly 88 fold".

As was stated earlier in this discussion of the
standard, no means was found of avoiding discrepancies in vol-
umes of compared manometers under low pressures. It is reason-

ably certain however, that these are due to variations of ca-
pillary depressions. And since no way of ascertaining these
was at hand without opening the manometer and experimentally
determining the depressions the "standard" was discarded.
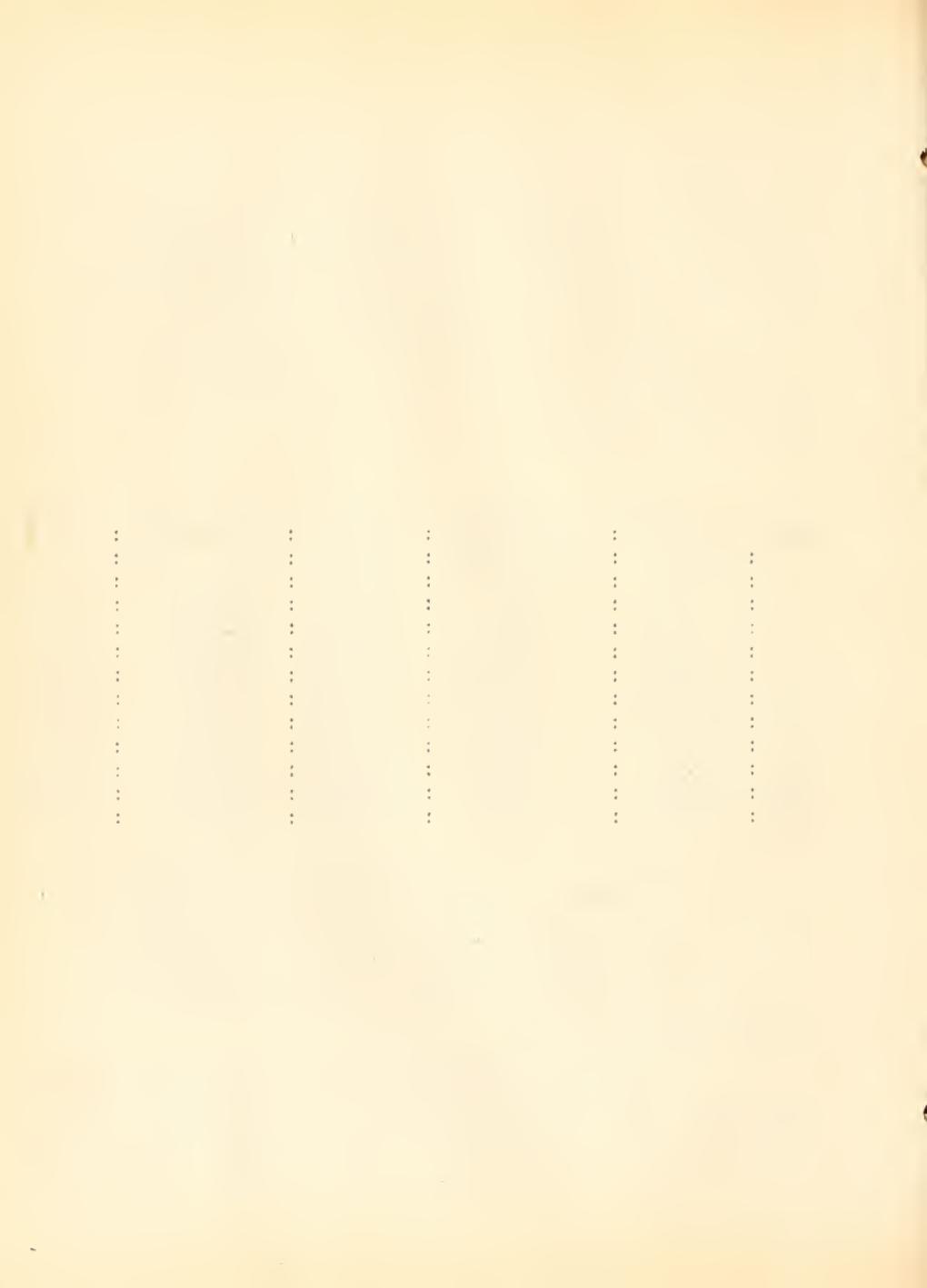
The next method used was that of "side tube". This
side tube consisted of a piece of tubing cut from the same piece
of tubing as the manometer itself, the object being, as has been
stated, to avoid capillary depression corrections. In some
instances concordant volumes were obtained from several obser-
vations. The range of pressures were necessarily limited, as
has been explained before. But even though this narrow range of
pressures, too wide variations were frequently found to be ascribed
to errors of observation. It was found that the errors of capil-
lary depression in the manometer tube and the side tube of pre-
sumably the same bore were in a great majority of cases, if not in
fact always, additive. In such a case as that recited in table I,
errors arising in this way would render the manometer quite worth-
less, and the time spent in its preparation, as well as that in
its use, would be lost.

In order to avoid such liability to error in deter-
mining the volume of nitrogen under standard conditions, a side

tube 40 m.m. in diameter was adopted - the same tube, in fact, that was used in capillary depression determinations. One of these tubes was sealed on to a barometer tube of ordinary bore and about 60 c.m. length. The tube carried a stopcock so that the column of mercury might be maintained while changing manometers in the block. This tube is represented in **Fig. III.** Results obtained by use of this tube were highly satisfactory. The objections arose to its use however. It was impossible to vary the pressure even a few millimetres; and furthermore the constant insertion and removal of manometers to and from the "steel blocks" augmented the chance of accident and breakage, further the process was very slow. The method which proved most satisfactory of all, and that which was adopted, was the use of the wide side tube, by rubber tube connection with the manometer. In fact the same fashion after which capillary depression were determined - the difference being that now the manometer was closed where before it was open. Comparisons were made on manometers by the side tube method, using the capillary tube of presumably the same bore as the manometer, both in the steel block and by rubber tube connection, against the values obtained when the wide side tube was used both in the steel block and by rubber tube method. In the case of the narrow side

tube no satisfactory agreements in volume from several observa-
tions at different pressures could usually be obtained. With
the wide side tubes the agreement was quite satisfactory both
in the block and rubber tube, and furthermore these values agree
closely with each other. Having established the reliability
and expediency of the method, work was immediately carried through
on the entire lot of the new type manometer. The procedure was
briefly as follows. Manometer and side tube were connected by
means of the rubber tube. (In order to avoid refilling the side
tube and rubber tube at each change of manometers, a screw clamp
was used to close the rubber tube near the manometer stem before
removing the latter). In this operation care was taken to ad-
mit no air in/the stem of the manometer. Both side tube and
manometer were clamped firmly into position, and small mirrors
bound on at a suitable angle for reflection of light to the tele-
scope. A tapper was placed in position against the manometer;
and the whole system was then allowed to come to constant tempera-
ture of the bath. After temperature equilibrium had certainly
been established, and after effective tapping of the manometer,
the following observations were taken: Volume of gas in manom-
eter between the two menisci, barometric pressure and tempera-
ture, height of mercury column in the side tube above the lower
meniscus in the manometer, and the constant temperature of the

manometer house. After making the proper corrections and apply-
ing the gas laws, the volume of gas contained in the manometer
under standard conditions of temperature and pressure was ob-
tained. The pressure on the manometer could be varied in a
limited degree by raising or lowering the side tube. This fact
was of prime importance, for it made it quite possible to bring
the lower meniscus to a portion of the capillary in which its
depression was accurately known. On such days when much fluctua-
tion of the barometer took place, it was difficult to control
the exact position of the meniscus, for as atmospheric pressure
increased the mercury column in the manometer would rise, and
contrary, when the pressure of the atmosphere decreased, the
mercury column in the manometer would fall. In such cases the
curves plotted for the depressions usually furnished the neces-
sary data for the corrections. However, in a few instances
these failed. The latter fact was probably due to some varia-
tion of depression which had still escaped the very detailed
examination for the same. In such cases the side tube was rais-
ed or lowered until the meniscus in the manometer stood in a
portion of the capillary where the depression was more constant.

With the exception of two of the manometers of the new
type, all gave volumes, under standard conditions, of more than

1000 calibration units. And the largest volume of all was some what more than 3200 units. In the case of the old type of manometer it was possible to obtain at most only about 800 units, and in most cases the volumes ranged from three to five hundred units. Since the calibration unit is a linear unit, and not a cubical unit, it is obvious that the size of the capillary controlling the calibration unit would have no influence on the number of units, in so far as increasing or decreasing that number is concerned, if the bore was of the ordinary uniformity. Hence it was impossible to increase the number of units greatly except by lengthening the tube. This was impracticable, and was rendered unnecessary by the adoption of the new type of instrument.

In determining the volumes of manometers, it is impossible to get values agreeing any more closely, in fractions of calibration units, with the old type of manometer than with the new type. Hence, if the actual fractional agreement is as close in a manometer of large volume as in that of one of small volume, the percentage error in the one of large volume is much smaller than that in one of small volume. In most of these manometers, extreme variation of the maximum or minimum volume, determined by observation, from the mean of all the values varied from 0.03 to

0.1 per cent. The variations fall well within the limits of errors of observation.

COMPARISON OF MANOMETERS

One more step was taken before the manometers were considered ready for osmotic pressure work. And this step would prove the worth or unfitness of the instruments. They were compared against each other. That is to say, two manometers were connected in such a way that the gas volumes were under the identical compression. The comparisons to the present have been made at low pressures only.

In order to compare two manometers against each other, at low pressures, they were connected by the same rubber tube used in the methods for determination of capillary depressions and volumes. Instead of side tube and manometer, there was now placed manometer and manometer. The same precautions were used, as before, to see that the rubber tube and stems of manometers were entirely filled with mercury and free of air bubbles. By adjustment of one of the manometers, up or down, the menisci of each could usually be brought to a desired point on the short capillary. Tappers were set in position against the instruments

and the system allowed to come to the constant temperature of the manometer house. The procedure of observations was identical with that in the determination of volume, except no barometer readings were necessary.

Obviously, when corrections for difference in height of the mercury columns in the two manometers, and capillary depressions, are applied, the pressures on both volumes of gas must be identical. And if the values for the volumes, obtained by the method set forth in this paper, are correct, then the calculated pressures from these volumes should be identical.

Those three manometers which showed, at once, smallest variation in calibration corrections, capillary depression, and percentage variation from mean in volume, were chosen as standards of comparison. These three are known respectively as numbers 31, 40 and 41.

In table II are shown a series of results obtained. The columns respectively represent the following: (1) the number of the manometer; (2) the value of the gas volume in the manometer under standard conditions, the value being obtained by the method described in this paper; (3) the observed volume of the slightly compressed gas; (4) the corrected pressure in millimetres calculated upon the assumption that the value in column 2 was correct; (5) corrected pressure expressed in atmospheres,

(6) the volume at standard conditions, calculated from pressure
of the other manometer as a standard; (7) percentage expression
of variation from original value of volume; (8) percentage er-
ror distributed between the two manometers.

TABLE II

1	2	3	4	5	6	7	8
(31 :	1204.53 :	1038.87 :	894.03 :	1.176 :	1200.62 :	0.32 :	0.16
(34 :	954.66 :	895.10 :	890.88 :	1.172 :	958.06 :	0.35 :	0.17
(40 :	1103.75 :	947.10 :	933.31 :	1.234 :	1103.75 :	0.00 :	0.00
(32 :	1212.88 :	1079.77 :	938.27 :	1.234 :	1212.88 :	0.00 :	0.00
(41 :	1676.64 :	1682.46 :	832.40 :	1.096 :	1677.40 :	0.05 :	0.03
(36 :	1302.19 :	1154.77 :	832.78 :	1.096 :	1301.68 :	0.04 :	0.02
(31 :	1204.53 :	1063.73 :	945.86 :	1.244 :	1201.14 :	0.23 :	0.14
(40 :	1103.75 :	959.98 :	946.21 :	1.241 :	1106.70 :	0.27 :	0.13
(32 :	1212.33 :	1112.52 :	803.73 :	1.091 :	1212.05 :	0.07 :	0.04
(41 :	1676.64 :	1689.69 :	809.96 :	1.090 :	1677.90 :	0.06 :	0.03
(31 :	1204.53 :	1072.29 :	894.56 :	1.177 :	1201.91 :	0.22 :	0.11
(32 :	1212.36 :	1135.57 :	892.16 :	1.174 :	1216.14 :	0.26 :	0.13
(41 :	1676.64 :	1697.35 :	825.01 :	1.086 :	1701.81 :	1.50 :	0.75
(30 :	1407.55 :	1294.37 :	837.40 :	1.101 :	1388.49 :	1.35 :	0.67

It will be noticed in the table above that manometer
32 was compared against each of the three chosen standards. It
agrees quite exactly with numbers 40 and 41, and agrees very
closely with number 31. Furthermore numbers 31 and 40 were com-
pared against each other and agree very satisfactorily. Such a
method of procedure makes it possible to place all the instru-
ments on the same basis.

Seventeen of the new type manometers were carried
through the operations described in this paper. Out of the
seventeen two(Nos. 25 and 30) are looked upon with suspicion.
In table II is given the reason for suspecting some error in
Number 30. The volume, as calculated for column 6, is far too
small to be accounted for through experimental error, and since
number 41 is in such close accord with the other manometers, it
is but the natural and necessary course to regard the value
in column 2 for manometer 30 as wrong. Number 25 presents a
similar discrepancy, although of small magnitude. However the
errors are too large to warrant the use of the manometer, in both
cases, in osmotic pressure work, until their nitrogen volumes,
at standard conditions, have again been carefully determined.

Any percentage error in volume, as expressed in column

7 of table II, is the whole error of the two manometers. Now,
since the two manometers are connected by free-flowing mercury,
the case is not unlike that of a balance. If one arm of the
balance moves in one direction, the other arm moves in the con-
trary direction. Then, in the case of the two connected manom-
eters, even a small displacement of equilibrium, for any cause
whatsoever, would divide itself between the two instruments.
Therefore it is unfair to make one monometer carry the error
of the two. For this reason the writer believes that column 3
expresses the real error more closely than column 7.

The comparisons of these manometers will be carried
on under pressures as high as 28 to 30 atmospheres. For this
work the "steel block" and the "brass block" will be used. The
brass block differs from the steel block in that its reservoir
contains water, and that manometers may be placed into it in
the same fashion as they are placed in the cells for an osmotic
pressure measurement.

SUMMARY

1. The earlier work on manometers has been reviewed,
and its inaccuracies taken into account.

2. A new type of manometer has been devised. Its ad-
vantages over the older type have been pointed out and discussed.

3.   The method of calibration of these manometers has
been reviewed.

4.   A supply of very high grade mercury has been pre-
pared and the method described.

5.   The method of determining capillary depressions of
the manometer tubes has been dealt with and the purpose fully
discussed.

6.   A review of the method for filling the manometers
with nitrogen, and of closing the instruments has been given,
and the method of preparation of the nitrogen gas has been de-
scribed.

7.   The apparatus, bath, and method of calculation for
determination of gas volumes, at standard conditions, of the
manometers has ben described.

8.   Comparisons of all the new manometers have been made
against each other at low pressures; and 15 satisfactory in-
struments have been obtained.

9.   The object of the work was to throw light on error
sources of manometers of small bore. Although much remains yet
to be done, it is believed that some progress toward the end
has been made.

BIOGRAPHY

The writer was born on a farm, six miles west of Brooksville, Mississippi, on May 10th, 1884. He was awarded the B. S. degree, from Mississippi College, Clinton, Miss., in June 1904; A. M. Ibid 1905. He has spent three years in residence in the Johns Hopkins University.